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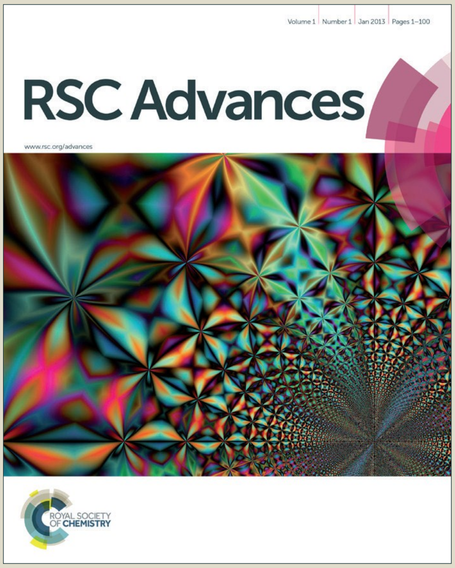

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Impact of Maximum Foam Reaction Temperature on Reducing Foam Shrinkage

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One of the obstacles to displacing petroleum-based polyols with soy-based polyols in rigid urethane foam formulations is foam shrinkage, especially at displacements greater than 50%. The shrinkage is a result of partial vacuums forming in the closed-cell foam as reaction temperatures dissipate. It was hypothesized that the shrinkage was in part due to inadequate curing of the foam which was due to lower maximum-attained temperatures during the near-adiabatic foaming process. Foam formulation studies were performed to evaluate the correlation of peak temperature foam shrinkage. Two approaches were evaluated to increase peak temperatures: a) preheating of the monomers prior to reaction and b) use of bio-based glycerol as a co-reagent to increase the mixture hydroxyl number and respective maximum temperatures. The results show that as the maximum reaction temperature increases, foam shrinkage decreases. Both preheating and use of glycerol co-reagent were effective for increasing peak temperatures and decreasing shrinkage. Experimental results were supplemented with simulation of the foaming process to better understand the fundamental phenomena and to evaluate the effectiveness of simulation to evaluate approaches to better utilize bio-based monomers in thermoset polymers.

Keywords: Polyurethane, soybean, polyol, simulation, catalyst, shrinkage, density.

Introduction

Polyurethanes (PU) are one of the highest value polymer markets because of their versatile and high-performance in applications ranging from furniture cushions to building insulation. 12 million metric tons of PU is consumed globally with an average annual growth rate of 5% [1, 2]. A 2007 US Presidential Green Chemistry Challenge award went to the development of soy-based polyols for use in PUs. Due to the high value of polyols, the good performance of soy-based polyols, and the size of the PU market; the PUs industry represents one of the largest sustainable green chemistry markets.

The major chemicals applied in the manufacture of PU foams are polyols, isocyanate, physical and chemical blowing agents, gel and blowing catalysts, surfactant, and cross linker.

The PU reaction is described in equation 1 (where R contains additional isocyanate moieties and R' contains additional hydroxyl moieties) in which the isocyanate is reacting with alcohol groups in the polyol(s) to produce the PU. To get foam, PU is expanded by either physical or chemical blowing agents or both. Water is normally used as a chemical blowing agent to produce carbon dioxide gas. The water-isocyanate reactions are described in equations 2 and 3.

$RNCO + R'CH_2\,OH \rightarrow RNHCOOCH_2R'$ eq. 1

Isocyanate + Alcohol → PU

$RNCO + H_2O \rightarrow RNHCOOH$ eq. 2

Isocyanate + Water → Carbamic Acid

$RNHCOOH \rightarrow RNH_2 + CO_2 + HEAT$ eq. 3

Carbamic Acid → Amine+Carbon Dioxide

In polymer chemistry, polyols are defined as the polymeric compounds containing at least two hydroxyl functional groups. These polyols will typically have molecular weights between 500 and 5,000. The properties of polyols, such as hydroxyl number, functionality, and molecular weight, play a significant role in determining the final properties of foams [3]. Polyols are characterized by functionality, hydroxyl number, and

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equivalent weight [4] as well as other properties that may be more specific to application.

PU producers are seeking to replace petrochemical based polyols by “greener” renewable materials due to the increasing in crude oil price and the strong public desire for environmentally friend products. Soy-based material is an excellent choice because it provides environmental and costing benefits in addition to performing well in PU polymers [5, 6]. Several excellent soy-based polyols are commercially available.

Partial substitution of petroleum-based polyols with bio-based polyols was studied by several researchers [7-9]. Fan measured different properties of PU rigid foams with partial substitution of soybean oil-based polyol [10]. The results show that a 50% substitution is the best to achieve good foam properties.

Suqin et. Al. [11] studied cell structure, cell size, density, thermal conductivity, and compressive strength when replacing polypropylene-based polyol with soy-based polyol. The results show that the density was within 5% of the controls, except that the density of foams from 100% soy-based polyol was 17% higher.

A reoccurring results of research on using soy-based polyols in PU foams is that displacing > 50% of the petroleum-based polyol in the formulation leads to deteriorating performance.

The goal of this work is to better understand how to fully displace petroleum-based polyols in a rigid foam formulation with bio-based polyols. A205, which is prepared by reaction of epoxidized soybean oil with ethylene glycol in the presence of catalyst, is used in this study [12, 13].

It is hypothesized that the lower hydroxyl number of A205 led to lower peak temperatures during reaction and that the lower peak temperatures led to inadequate curing. Insufficiently cured foams may have inadequate strength to resist the tendency to shrink caused by partial vacuums which form in closed cells of rigid foams—closed cells are important for good insulating properties. An understanding of the fundamental cause for inferior performance of a foam is an important step toward providing variations in formulations and processes (e.g. preheating) to fix the problems.

The soy-based polyol industry has undergone a significant evolution during the past two decades. In the early 1990’s, a few customers were content with simply displacing 5-10% of the polyol in the formulation where, often times, the soy-based component acted more like an inert component or plasticizer than a monomer. During the next 15 years, several good-performing soy-based monomers were developed and have become commercial; however, the mind-set of much of the industry was to require “drop-in” substitutions for the commercial petroleum-based polyols.

Soy-based drop-ins for petroleum-based polyols is a particularly problematic goal since petroleum-based polyols are custom-built from 2-4 carbon oxides (ethylene, propylene, and butylene oxide) to attain specific structures known to deliver the desired performance. The cost-effective soy-based polyols retain much of the soybean oil backbone, and so, it is simply not possible to custom-design structures.

An alternative approach to “drop-in” substitutes is the combination of soy-based polyols and simulation software to rapidly identify how to modify a PU formulation to provide similar performance. Simulation is necessary because PU formulations tend to have many more degrees of freedom as used to specify the thermoset formulation as compared to thermoplastic formulations. Typically eight or more degrees of freedom are used in specifying foams that include monomer selection and their concentrations, two or more homogeneous catalysts, blowing agent(s), and additives. The status of PU foam formulation is more of an art than a science. Simulation can be used to transform the industry to more of a science than an art, and can be an important enabling technology to green chemistry in the PU industry.

The simulation presented in these studies is based on a simultaneous solution of over two dozen ordinary differential equations [14] for the many reaction and physical processes that occur in the foaming process. Simulation of the reaction temperature quantifies the factors impacting peak temperature and to assists in identifying conditions that produce desired temperature profiles.

Methodology

Experimental design

Gel and foaming experiments were performed to create PU gel and foams as described in the following steps:

1. Weighed masses of polyols, fire retardant, catalysts, surfactant, chemical blowing agent, and the physical blowing agent are added together as a B-side in a plastic cup and mixed for 10 to 15 second in a 2000 rpm mixer.
2. Via a syringe (weighed before and after), isocyanate (as A-side) is added to the mixture and the new mixture is mixed with a 2000 rpm mixer for 10 seconds.
3. The mixture of A and B-sides is quickly poured into wooden mold (11.4×11.4×21.6cm) with aluminium foil lining to measure temperature profile.

A thermocouple is inserted into the center of the foaming PU. Temperatures and times were recorded by LabVIEW software.

To control preheating of monomers and all items contacting the PU reaction mixture, a temperature-controlled oven equipped with mixing capabilities through a rotating shaft that enters the oven’s top. The oven is used to preheat A- and B-sides, mixing blade, the thermocouple, and the foaming box with foil inside for about one hour. A 35 and 45°C were chosen as pre-heating temperatures because they provide enough distinct results for evaluating the impact of preheating and high enough to avoid blowing agent from evaporation.

Materials and Recipes

Gel Experiments

Control – A commercially available 490 hydroxyl number polyol (V490) was selected as a control in this study.

A205 Gels - A205 polyol is synthesized by reaction of epoxidized soybean oil with ethylene glycol in the presence of toluene sulfonic acid in a controlled temperature of 161°C. The epoxy number of A205 is around 1.3 and its water content is 0.2 % [15]. The amount of A205 is calculated so that it has the same total moles of hydroxyl functional group as the control.

A205/Glycerol Study – Adding glycerol as a polyol co-reagent (hydroxyl number = 1829[16]) was used as an alternative method to increase the maximum reaction temperature of the A205 polyol.

Glycerol has a 66.67% primary and 33.33% secondary alcohol moiety fractions. The amount of glycerol is calculated so the resulting A205/Glycerol mixture has the same total moles of hydroxyl functional group as the control. Glycerol was chosen because it is available as bio-based.

An isocyanate index of 1.1 is used in all the gel systems above except for the control (0.9) to avoid excessively high peak temperatures.

The properties of the control, A205, and isocyanate are summarized in Tables 1. Table 2 provides the recipe of the gel reaction using the control, A205, and A205/Glyceren mixture.

Table 1. Specifications of V490, A205, and isocyanate.

Property	V490	A205	Isocyanate (PMDI
Density, g/cm3	1.11	-	1.23
Average molecular weight	460	-	340
Functionality	4.3	-	2.7
Hydroxyl number, mg KOH/g	484.8	200	-
Equivalent weight	115	280.5	134
Viscosity, mPa.s at 25°C	6180	-	150-220
NCO content by weight, %	-	-	31.4
Vapor pressure, mm Hg at 25°C	-	-	<10-5
Specific heat, gm.cal/gm.at 25°C	-	-	0.43

Table 2. Gel reaction Recipe of the control (V490), A205, and A205/Glycerol mixture.

Ingredients	**Weight, gm**		
B-side materials	Control	A205	A205/Gly.
V490	32.2	0	55
A205	0	78.86	0
Glycerol	0	0	2.5
Dimethylcyclohexylamine (Cat8)	0.12	0.12	0.12
Pentamethyldiethylenetriamine (Cat5)	0.32	0.32	0.32
A-side material			
Isocyanate (PMDI)	41.58	41.58	41.58

Foam Experiments

While the final PU application is as a foam, gel tests were performed to evaluate performance without the added reaction and physical process complexities of foam processes. Evaluation of both provides for greater insight and certainty.

Foam experiments were performed for the three gel formulations by adding blowing agents and blowing catalysts. The amounts of the fire retardant, surfactant, and the blowing agent are the same for all the systems. Also, a 1.1 isocyanate index is used for all the system except for the control (0.9) to avoid excessively high peak temperatures. The amounts of catalysts used are also the same except for the gels and foams with the preheating attempt (catalysts loading studies). The recipes of these foams are shown by Table 3.

Foam shrinkage is measured using water displacement method. This method provides good accuracy for measuring the volume of un-regular shapes. Since the foam prepared is a closed-cell, the amount of water absorb by the foam is neglected. Foams were cut in regular shapes to measure the initial volume, and then the water displacement method was used to measure the new volume after shrinkage. Foam density was measured using the volume and weight of the foam samples.

Table 3. Foam reaction Recipe of the control, A205, and A205/Glycerol mixture.

Ingredients	**Weight, gm**		
B-side materials	Control	A205	A205/Gly.
V490	32.2	0	0
A205	0	78.86	55
Glycerol	0	0	2.5
Dimethylcyclohexylamine (Cat8)	0.12	0.12	0.12
Pentamethyldiethylenetriamine (Cat5)	0.32	0.32	0.32
Momentive L6900	0.6	0.6	0.6
TCPP	2	2	2
Water	1.04	1.04	1.04
Methyl Formate	2.4	2.4	2.4
A-side material			
Isocyanate (PMDI)	48.06	58.74	58.74

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (FEI Quanta 600) is used to examine foam cells morphology of the control, A205 prepared at ambient temperature, and A205/Glycerol. Foams were cut using a razor blade into a 10 x 10 x 1 mm slices and attached to the stub using conductive carbon tape. Slices were sputter coated with thin layer of platinum and imaged at an accelerating voltage of 5 kV and x80 magnification. The cellular structure of the foams was observed parallel to the free-rise direction.

Results and Discussion

Figures 1 and 2 show the experimental and simulated temperature profiles for the gel reaction control and gel reaction with 100% displacement of the control polyol with A205. The initial temperature of 22 °C indicates no preheating was used.

Whereas the model line for the control formulation was generated using kinetic and physical parameters(pre-exponential factors, Activation energies, and Heat of reactions) as previously reported[14], the model line for A205 was based on parameters fitted the data and a hydroxyl number obtained by titration of the polyol. The fitted parameters included fraction of primary, secondary, and hindered secondary of alcohol moieties. This approach was previously published [17] and represents a method that both reduces the number of parameters needed to characterize a polyol and provides for immediate insight into the reactivity and structure of the polyol. Fractions of 50% primary, 50% secondary, and zero hindered secondary moiety fractions provided the best-fit characterization of A205.

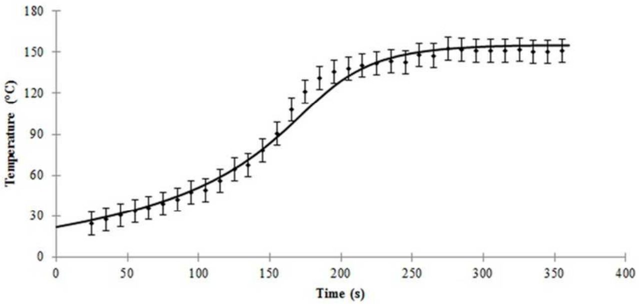

Figure 1. Temperature profile of PU gel reaction control. Symbols “♦” represent experimental data and the solid line represents simulation results.

Since repeating the experimental data show very slight change from system to system, there is no reason to expect significant changes when repeating experiments for in the next experiments.

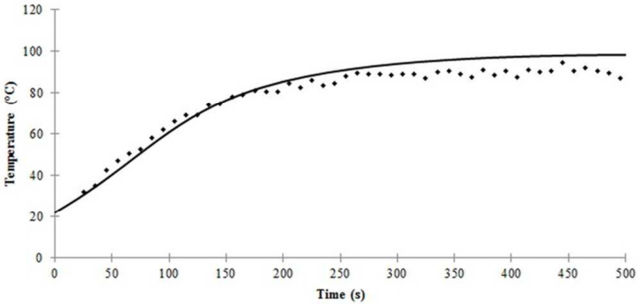

Figure 2. Temperature profile of PU gel reaction using A205. Symbols “♦” represent experimental data and the solid line represents simulation results.

Once the A205 polyol was characterized (fit of Figure 2), the fitted parameters were used in the simulation program to project the impact of preheating and glycerol addition on performance. The simulation results and experimental data are provided by Figures 3 and 4. There was good agreement between what was predicted by the simulation software and the super-imposed experimental data for the gel reactions.

Preheating leads to substantial increases in initial reaction rates and more-rapid attaining of maximum temperature. In addition, increasing the initial temperature increases the maximum temperature of the reacting mixture. The presence of glycerol leads also to increase the initial reaction rates because it has highly reactive primary hydroxyl group and high heat of reaction.

The trend of the temperature profiles of the A205 is prominently different than that of the control (V490). This is likely attributed to using ethylene glycol as a reagent in the synthesis of A205. If only one of the alcohols of ethylene glycol reacts, the other remains as a primary hydroxyl with a high reaction rate; it is likely that this primary hydroxyl (corroborated by fitted parameters) is present and leads to high reaction rates. Also, the existence of ethylene glycol in synthesizing leads to a special A205 structure and/or reaction activity.

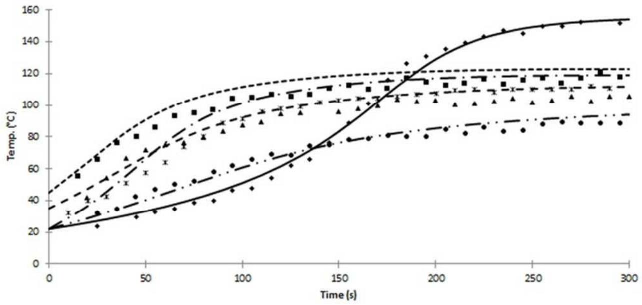

Figure 3. Effect of preheating monomers of PU gel reaction using A205 or A205/glycerol as polyol on the maximum heat of reaction. Symbols “♦, ●,▲,■,,×” represent experimental data using V490, A205 at ambient temp., 35, and 45˚C, and A205/Glycerol respectively. Lines from higher to lower peak temperature represent simulation results using V490, A205 at 45°C, A205/Gly. at amb. temp., A205 at 35°C, and A205 at amb. Temp. respectively.

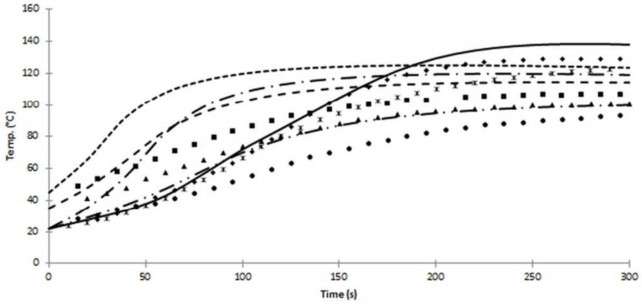

Figure 4. Effect of preheating monomers of PU foaming reaction using A205 or A205/glycerol as polyol on the maximum heat of reaction. Symbols “♦,●,▲,■,×” represent experimental data using V490, A205 at ambient temp., 35, and 45˚C, and A205/Glycerol respectively. Lines from higher to lower peak temperature represent simulation results using V490, A205 at 45 ˚C, A205/Gly. at amb. temp., A205 at 35 ˚C, A205 at amb. temp. respectively.

Figure 3 illustrates how higher hydroxyl numbers (V490 and glycerol) as well as preheating lead to higher peak temperatures. The hydroxyl numbers are 484.8, 205.24, and 1829 for V490, A205, and glycerol.

The gel simulation results fully corroborate the temperature trends and the maximum temperatures. The slight variation in the trends results from the uncertainties in heat capacities and heats of reaction.

As compared to gel reactions, temperature rises for foam-forming reactions are faster and this attributed to the heat of reaction between water and isocyanate. For the foam reactions, the simulation predicts the temperature rise to be faster for several of the systems than the experimental data (Figure 4). A further inspection reveals that when the model predicts substantial temperature increases (e.g. >30% of the maximum temperature increase) in the first 50 seconds, the model projects a more rapid rate of increase than the data. This can be attributed to the fact that the model is based on Arrhenius-type reaction kinetic models, and in highly viscous reaction systems mass transfer can limit reaction rates as opposed to limits on reaction rates.

Addition of diffusion rate limitations to reaction kinetics is outside the scope of this work, and so, an alternative approach was taken. The alternative approach consisted of adjusting recipes (lowering catalyst concentrations) to mixtures where diffusion would not limit reaction rates.

Catalyst Loading Study

The soy-based A205 is more reactive than the control petroleum-based polyol. This insight reveals a previously unknown benefit of the soy-based polyol; the higher intrinsic reactivity would allow lower catalyst loadings to be used. Catalysts are a major contributor to the costs of many urethane foams.

Quantifying the extent to which the amount of catalyst for the A205 gels and foams can be reduced was performed using the simulation software. Catalyst loadings were reduced until the temperature reaches its half value (half of increase at peak temperature) at the same time when the temperature profile of the control reached its half value. Figures 5, 6, and 7 show how the amounts of catalysts are achieved for different initial preheating temperature. Table 4 shows the different amounts of catalysts loadings obtained at different preheating temperatures.

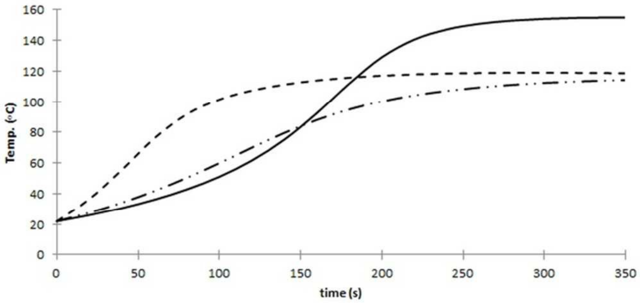

Figure 5. Temperature profile of A205 at ambient temperature (22°C) to achieve low catalysts loading. Lines from higher to lower peak temperature represent simulation results using V490, A205 at ambient temp. with full catalyst loadings, and A205 at ambient temp. using low catalyst loadings respectively.

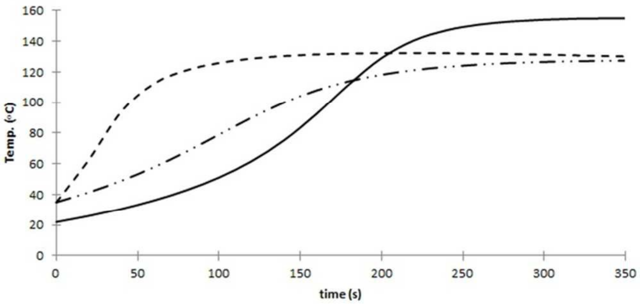

Figure 6. Temperature profile of A205 at 35°C to achieve low catalysts loading. Lines from higher to lower peak temperature represent simulation results using V490, A205 at 35˚C temp. using full catalyst loadings, and A205 at ambient temp. using low catalyst loadings respectively.

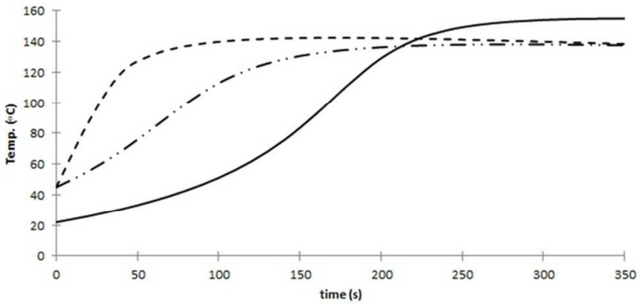

Figure 7. Temperature profile of A205 at 45°C to achieve low catalysts loading. Lines from higher to lower peak temperature represent simulation results using V490, A205 at 45˚C temp. using full catalyst loadings, and A205 at ambient temp. using low catalyst loadings respectively.

Table 4. Catalysts loadings of the A205 gels and foams at different preheating temperatures.

Catalysts	Weight, gm		
	At ambient temp. (22°C)	At 35°C	At 45°C
Dimethylcyclohexylamine (Cat8)	0.072	0.036	0.012
Pentamethyldiethylenetriamine (Cat5)	0.192	0.096	0.032

Figure 8 present both experimental and simulation temperature profiles of the gel reaction using the control, A205, or A205/Glycerol as polyol at different preheating temperature and the new catalyst loadings of Table 10. Figure 9 shows foaming experiments for the new catalyst loadings.

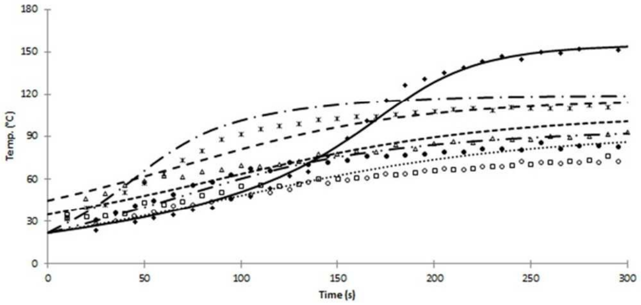

Figure 8. Temperature profiles of PU gel reaction of the using the control (V490), A205, or A205/Glycerol as polyol. Symbols “♦,●,○,□,Δ,×” represent experimental data using V490, A205 at ambient temp. with full catalyst loading, A205 at ambient temp., 35, and 45˚C with low catalysts loading, and A205/Glycerol respectively. Lines from higher to lower peak temperature represent simulation results using V490, A205/Gly. at amb. temp., A205 at 45˚C with low cats, A205 at 35 ˚C with low cats, A205 at amb. temp. with full cats, and A205 at amb. temp. with low cats loading respectively.

For foam-forming system, simulation is in better agreement with data when half temperature times are greater than 100 seconds. The simulation is successful both quantifying the impacts on reaction temperature profiles at conditions where mass transfer does not slow down the reaction. Even when mass transfer is the rate limiting step, the simulation provides qualitative trends.

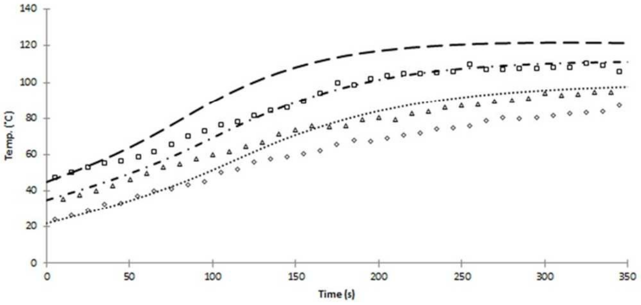

Figure 9. Temperature profiles of PU foaming reaction of the using A205 as polyol. Symbols “◊Δ□” represent experimental data at ambient temp., 35, and 45˚C respectively with low catalyst loadings. Lines from higher to lower peak temperature represent simulation results using A205 at 45˚C with low cats, A205 at 35 ˚C with low cats, and A205 at amb. temp. with low cats respectively.

The following advantages were realized for simulation as a tool for use in urethane formulation development, simulation provided:

- Insight into when mass transfer limitations on reaction kinetics become limiting,
- Insight into the type of hydroxyl functional groups (primary versus secondary) and how these groups impact reaction.
- A quantification of the trade-off between pre-heating and catalyst addition to achieve desired reactivity profiles.
- A quantification of peak temperatures of the foam as a function of formulation.

Density and Shrinkage Study

It was observed that the foam of the A205 formulation of Figure 4 exhibited considerable shrinking (with associated increase in foam density) during the time frame of 30 minutes to 6 days. A first method to reduce shrinkage, no cutting of the foam was performed until after day five; this led to a substantial reduction in shrinkage but not an elimination of shrinkage.

The foams prepared from A205 at ambient temperature (with full catalysts loading) have low peak temperatures (figure 9) and high shrinkage due to the low hydroxyl number of the polyol. An advantage of the lower hydroxyl number is a reduced isocyanate content in formulations (green chemistry). Disadvantages include reduced peak temperatures and less cross linking in the polymer.

Preheating to 35 and 45ºC (with full catalysts loading) reduced the shrinkage. Figure 10 illustrates how the percent shrinkage appears to be directly related to the maximum reaction temperature. Increases in peak temperature lead to faster reaction rates and more-complete curing during the timeframe when shrinkage occurs.

To verify how the higher peak temperature leads to more-complete curing, figure 10 shows the urethane moieties resulting from polymer-polymer reactions for the different systems. The polymer-polymer reactions constitute a crosslink density and ultimate curing. Later onset of the crosslinking or a lower crosslinking density results in a foam that can shrink when the temperature of the foam cools. By comparing this figure with the results shown in figure 3, its obvious that at higher peak reaction temperature more urethane moieties produced from the polymer-polymer reaction and this is interpreted to faster crosslinking.

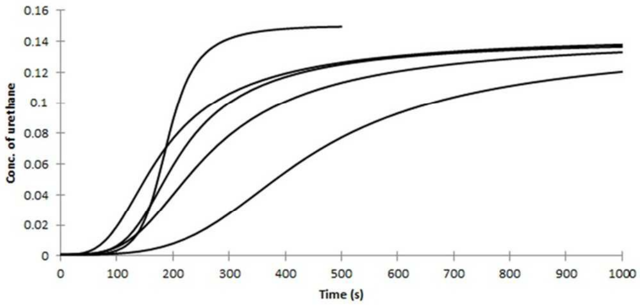

Figure 10. Urethane concentration from the polymer-polymer reaction. Lines from higher to lower concentration represent simulation results using V490, A205 at 45˚C, A205/Gly. at ambient temperature, A205 at 35 ˚C, and A205 at ambient temperature respectively.

This exemplifies how the “setting” of the foam is different from the “curing” of the foam. Setting of the foam occurs when an adequate resin structure exists to prevent collapse; however, that resin structure may still be too week to withstand the vacuum forces that can form inside the closed cells. Curing can lead to further crosslinking and a sufficiently strong resin to withstand the vacuum forces without shrinkage. In addition to time and temperature to attain an adequate amount of curing, foam formulation must provide enough cross-linking capability and rigidity (hard segments, high glass transition temperature) for a rigid resin structure.

Figure 11 shows the relationship between precent shrinkage and the maximum reaction temperature for the A205 foams at different preheating temperatures and different catalyst loadings. It is obvious that the foams with the full catalyst loadings have less shrinkage due to the higher maximum reaction temperature and higher catalyst content that may have cross linking effect.

Figure 12 compares densities of the A205 foams at different preheating temperatures and different catalysts loading. Differences in density between foams of different catalysts loadings decrease with increased preheating.

Table 5 summarizes the values of percentage shrinkage and both density measurements. The values show that foams tend to have less changing in density (see Figure 13) and less shrinkage values when using higher hydroxyl number polyols like V490 and A205/Glycerol.

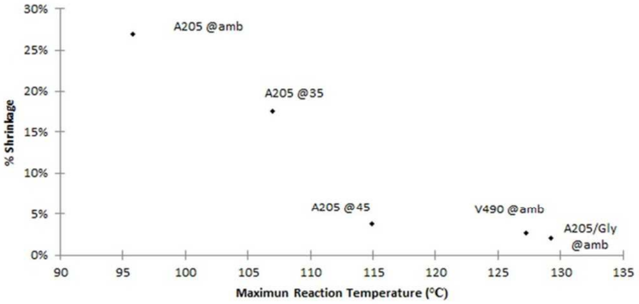

Figure 11. The relationship between the peak temperature of foaming reaction and shrinkage percentage for foams using the control, A205 and A205/Glycerol at different preheating temperatures with full catalyst loadings.

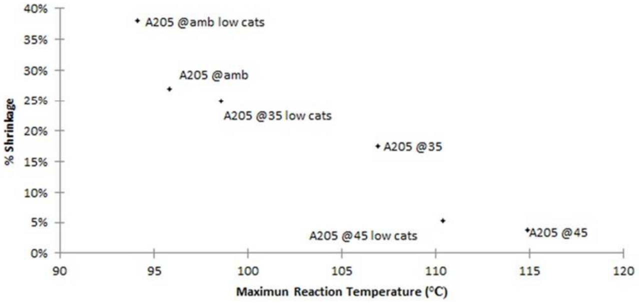

Figure 12. The relationship between the peak reaction temperature of foaming reaction and shrinkage percentage for foams using the control, A205 andr A205/Glycerol at different preheating temperatures and different catalyst loadings.

Simulation results effectively predicted the impact of preheating and glycerol addition on the peak reaction temperature of the foams. Simulation also quantified the trade-off between preheating and more catalyst addition. At this point in its development, preheating is not able to predict shrinkage from fundamentals; however, empirical correlations based on trends of Figures 10 and 11 are possible.

Table 5. Values of % shrinkage and % density change for A205 foams at different preheating temperature and catalysts loadings.

Polyol used in Foam recipe	Max. Reaction Temp.	% Shrinkage	Initial Density	Final Density	% Density Change
V490 at amb	129.3	2.03	0.39	0.423	8.09
A205 at amb	95.8	26.92	0.175	0.212	21.53
A205 at 35 ˚C	106.9	17.58	0.114	0.125	9.33
A205 at 45 ˚C	114.9	3.74	0.109	0.113	3.14
A205 at amb low cats	94.1	37.97	0.144	0.215	49.35
A205 at 35 ˚C low cats	98.6	24.89	0.181	0.235	29.87
A205 at 45 ˚C low cats	110.4	5.27	0.242	0.259	6.86
A205/Glycerol	127.2	2.69	0.459	0.475	3.54

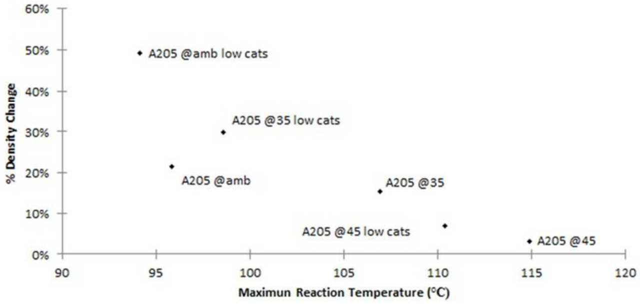

Figure 13. The relationship between the peak reaction temperature and percent density change for foams using the control, A205 andr A205/Glycerol at different preheating temperatures and different catalyst loadings.

The SEM images in Figure 14 shows that the cell structure of A205 prepared at ambient temperature has substantially more open-cell content and distorted cell structure as compared with the control. Increasing peak reaction temperature eliminates the distorted cell structure and result in a high closed cell-content.

It should be noted that the foams studied in this investigation were cured prior to cutting. The foam skin sealed the exterior and allowed for open cell content to have minimal impact on shrinkage and to allow water displacement to provide accurate density measurement.

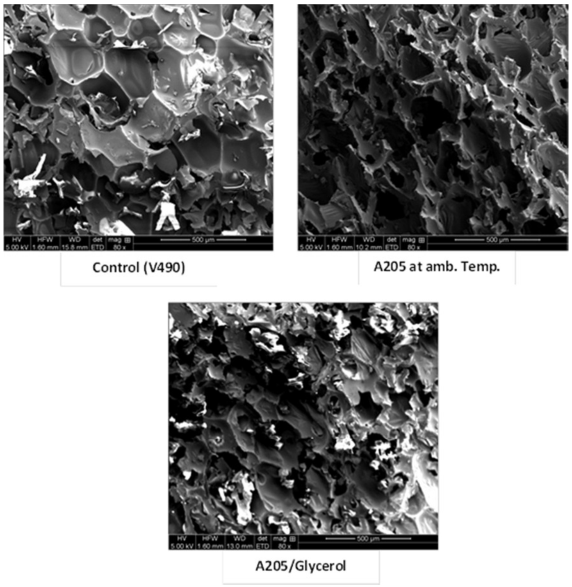
Control (V490)
A205 at amb. Temp.
A205/Glycerol

Figure 14.Scanning electron micrographs of the cut section of the foams showing the cell morphology

Conclusion

Simulation was a valuable tool in being able to develop formulations that allow 100% of the soy-based polyol to be used while avoiding shrinkage. The simulation quantified how higher reactivity of the soy-based polyol can be translated to lower catalyst loadings. Preheat can also be used to reduce catalyst loadings. Further studies are needed to evaluate the impact of these new formulations on thermal conductivity and compressive strength.

For these formulations, the maximum reaction temperature (peak temperature) attained during reaction was a critical performance metric that translated to reduced shrinkage of the foam. Two different methods were used to increase the peak temperature of reaction: a) preheating the monomers to a 35 and 45°C temperature which increased the initial rates of reaction and lead to a faster and higher maximum temperature and b) adding glycerol to the bio-based polyol to increase its hydroxyl number and the heat of reaction.

This is one of the first (if not the first) applications of simulation of the foaming process to assist in formulation modification to allow the use of bio-based polyols. Historically, the PU industry has pursued drop-in bio-based solutions to avoid the costs of reformulating PU recipes. Simulation provides a new and powerful green chemistry tool to reduce the costs of adopting new bio-based polymers in thermoset formulations.

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